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Living, Isoselective Polymerization of Styrene and Formation of Stereoregular Block Copolymers via Sequential Monomer Addition

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The living, stereoselective polymerization of olefins and diolefins has attracted in the past years many researchers for the unique possibility to synthesize polymers with well-defined stereochemistry, controlled molecular weight, and narrow molecular weight distribution and block copolymers with defined block length and sequence.[1]

Among the new polymers obtained by homogeneous catalysis promoted by transition metal complexes, the discovery by Ishihara et al. that the homogeneous catalysts composed of titanium halides or alkoxides, with an η^5-cyclopentadienyl (Cp) ligand, and methylaluminoxane[2] (MAO) promote the syndioselective polymerization of styrene has brought forth a growing interest in such material for its unique proprieties.[3] As consequence, the living, syndioselective polymerization of styrenic monomers has been investigated by many groups in order to obtain copolymers containing syndiotactic polystyrene blocks.[4]

In this area, the styrene−butadiene (SB) copolymers are of particular interest because of the stereoregularity of both blocks with respect to the commercially available SB and styrene−butadiene−styrene (SBS) triblock copolymer produced via a living anionic polymerization technology is expected to improve the mechanical and thermal properties. Despite the efforts devoted to the synthesis of such materials, the achievement of an efficient system able to produce stereoregular SB block copolymers under acceptable reaction conditions is still a challenge.[5]

The living, syndioselective polymerization of styrene and the formation of syndiotactic-polystyrene-*block*-*cis*-1,4-polybutadiene has been reported by Shiono and co-workers, who also succeeded in the synthesis of SBS triblock copolymers.[5] In this case, however, the polymerization reactions should be conducted at subambient temperature producing copolymers with a minor amount (10−20%) of amorphous polymer contaminant that should be extracted in THF.

Conversely, the isoselective polymerization of styrene received little attention, and only recently efficient homogeneous catalysts were developed for the synthesis of highly isotactic polystyrene-(*i*-PS).[6] Furthermore, the isoselective, living styrene polymerization also became possible in the past years by using a titanium complex bearing tetradentate [OSSO] bis(phenolate) ligand activated by $[PhNMe_2H][B(C_6F_5)_4]$ in the presence of $Al(nOct)_3$ at 25 °C, but no data concerning the formation of block copolymers have been reported to date.[7]

Herein we report the living stereoregular polymerization of styrene and butadiene promoted by the complex **1** activated by MAO and the formation of isotactic-polystyrene-*block*-1,4-*trans*-polybutadiene copolymer by sequential monomer addition.

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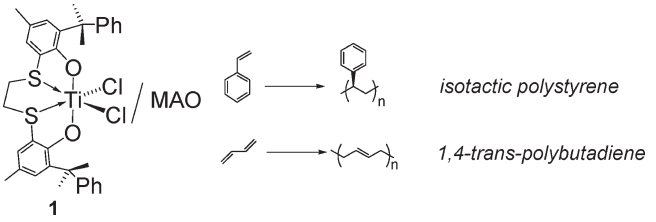
Scheme 1. Stereoregular Polymerization of Styrene and Butadiene with 1/MAO



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Scheme 1 depicts the polymerization of styrene and butadiene promoted by **1**/MAO under optimized conditions producing highly isotactic polystyrene (*i*-PS) and high 1,4-*trans*-polybutadiene(PB). The narrow molecular weight distribution and the observation that M_n increases linearly with styrene conversion clearly indicate a living behavior of the polymerization at room temperature (Figure 1). A similar behavior was also observed in the case of butadiene polymerization at 0 °C producing 1,4-*trans*-polybutadiene (PB) with a minor amount of *cis*-1,4-units (≤5%), but in this case a slight broadening of the molecular weight distribution with conversion was observed.[8]

It is worth noting that the bulky cumyl groups in the *ortho* positions with respect to the phenolate moiety are essential for the living polymerization of both monomers. As a matter of fact, the analogous titanium complex bearing *tert*-butyl groups in the same position produces polystyrene and polybutadiene with broader molecular weight distribution.[4e,6a] The effect of the steric hindrance of the *ortho* substituents on the of chain termination reactions (i.e., β-hydride elimination) has been already reported to be a key factor for the livingness of propene polymerization in a related class of postmetallocene catalysts.[9] The real utility of living polymerization is a possibility to synthesize well-defined block copolymers, creating new polymeric architectures with promising physical, mechanical, and chemical properties. To the best of our knowledge there are no examples of block copolymers incorporating *i*-PS or 1,4-*trans*-PB segments in the literature.

Owing to the living behavior and the high stereoselectivity of **1**/MAO for styrene and butadiene polymerization, we reasoned that it would make an ideal catalyst for the synthesis of block copolymers. The polymerization was conducted at 25 °C by sequential monomer addition, leaving the styrene reacting the necessary time for the complete monomer consumption before the addition of butadiene. The results are summarized in Table 1.

The yield is close, in any case, to the total conversion, and no broadening of the molecular weight distribution with polymerization time is observed. In analogy to that observed in case of the butadiene homopolymerization, the reactivity of this monomer is rather slow compared to styrene, and no total conversion of this monomer is reached in reasonable polymerization time. In any case, by judicious choice of the monomer composition in the feed one can fine-tune the relative length of the blocks obtaining in any case copolymers with high molecular weight and narrow molecular weight distribution, confirming for both the initial *i*-PS homopolymer and the final *i*-PS-*block*-1,4-*trans*-PB copolymer a living behavior. A representative GPC profile of the diblock copolymer and the profile of an aliquot of *i*-PS that was removed from the same polymerization mixture before feeding butadiene are shown in Figure 2.

The thermal features of the resulting copolymers have been investigated by means of differential scanning calorimetry (DSC).

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Table 1. Styrene−Butadiene Copolymerization Data by Sequential Monomer Addition with 1/MAO

run[a]	X_S (feed)	X_S (copolymer)[b]	conversion (%)	$M_n \times 10^{-3}$ (PS)[c]	M_w/M_n[c] (PS)	$M_n \times 10^{-3}$ (PS-*b*-PB)[d]	M_w/M_n (PS-*b*-PB)[d]	$T_{m,PB}$[e]/°C	$T_{m,PS}$[f]/°C
1	0.10	0.30	92	108	1.06	139	1.08	42.6/83.8	222.8
2	0.20	0.40	85	136	1.07	168	1.11	44.4/85.8	223.7
3	0.30	0.50	90	171	1.06	190	1.08	45.4/82.5	224.1
4	0.40	0.60	95	167	1.07	201	1.11	42.9/85.5	223.9
5	0.50	0.70	84	156	1.04	194	1.10	44.8/82.1	222.9
6	0.60	0.75	83	163	1.07	186	1.09	46.2/81.8	223.5
7	0.70	0.80	85	166	1.07	182	1.10	44.0/80.4	223.6
8	0.80	0.90	90	161	1.08	179	1.10	40.4/82.9	223.9
9	0.90	0.95	95	149	1.07	176	1.07	42.6/85.9	224.0

[a] Polymerization conditions: Ti = 1.0 μmol; [Al]/[Ti] = 1200; T_{run} = 25 °C; V_{tot} = 20 mL (styrene + toluene); styrene (13 mmol) and the proper amount of butadiene solution in toluene; polymerization time: 2 h (styrene) + 2 h (butadiene). [b] Determined from ^{1}H NMR spectra. [c] Relative to the isotactic polystyrene block before feeding butadiene monomer (for all the runs the M_n^{theo} is 135×10^3). [d] Relative to the isotactic-polystyrene-*block*-1,4-*trans*-polybutadiene. [e] Melting temperature relative to the 1,4-*trans*-polybutadiene block in the resulting isotactic-polystyrene-*block*-1,4-*trans*-polybutadiene, determined by 10 °C/min heating rate DSC scans. [f] Melting temperature relative to the isotactic polystyrene block in the resulting isotactic-polystyrene-*block*-1,4-*trans*-polybutadiene, determined by 10 °C/min heating rate DSC scans.

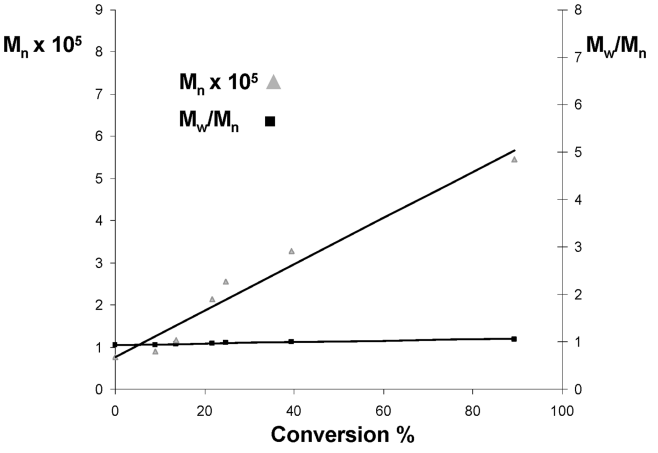

Figure 1. Plot of PS M_n (▲) and M_w/M_n (■) versus yield using **1**/MAO at 25 °C determined by gel permeation chromatography (PS standards).

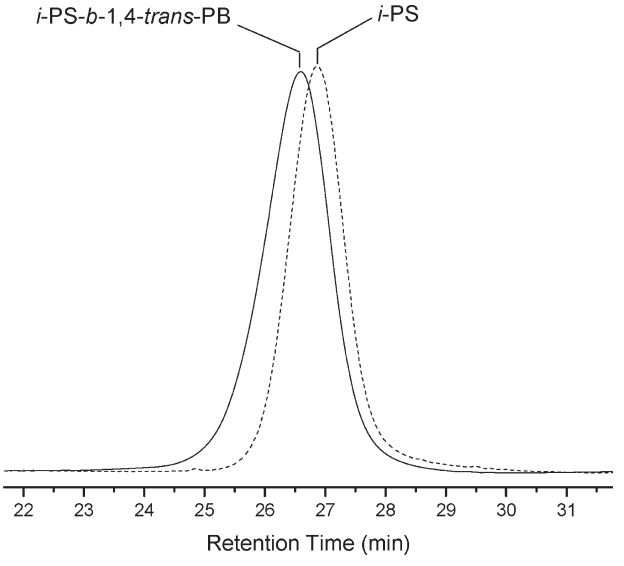

Figure 2. GPC profiles after the formation of the *i*-PS block before feeding butadiene and the final *i*-PS-*block*-1,4-*trans*-PB block.

In Figure 3, the DSC thermograms of i-PS-*block*-1,4-*trans*-PB block sample **1**, *i*-PS, and 1,4-*trans*-PB samples, obtained with the catalyst **1**/MAO, are reported as examples. The *i*-PS and 1,4-*trans*-PB homopolymers are crystalline. The comparison of DSC scans shows that both blocks in copolymer are

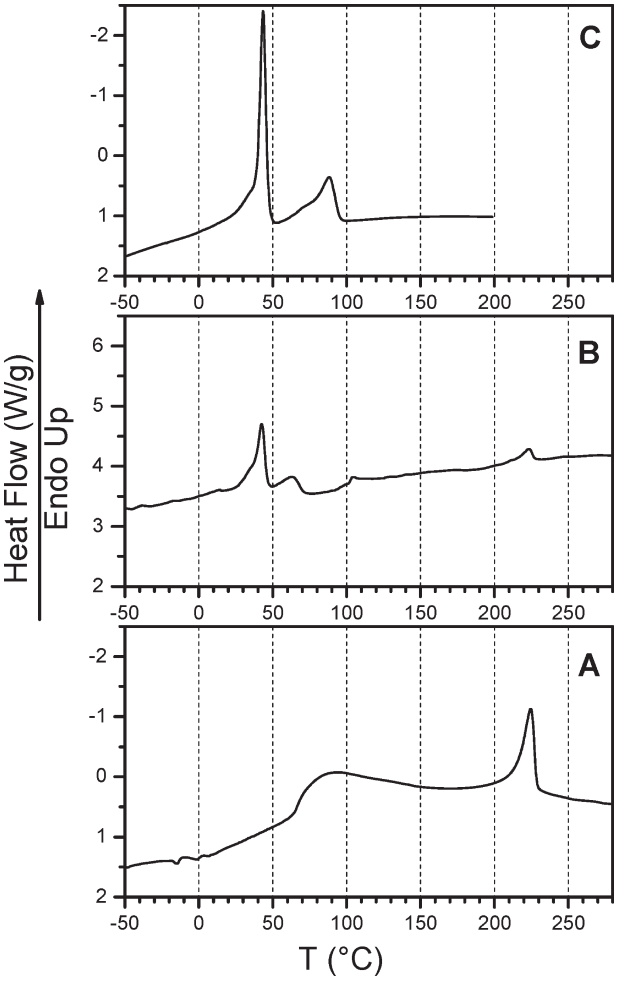

Figure 3. DSC scans at 10 °C/min heating rate of (A) *i*-PS, (B) *i*-PS-*block*-1,4-*trans*-PB-*block* copolymer sample **1**, and (C) 1,4-*trans*-PB obtained by using the catalytic system **1**/MAO.

crystalline with melting points values similar to that of *i*-PS (224.5 °C) and 1,4-*trans*-PB (46.9/87.8 °C) samples, respectively (see Table 1). It is worth reminding that the two endothermic peaks in the DSC thermogram of the 1,4-*trans*-PB correspond to the transitions from the crystal to the mesophase and from the mesophase to the melt.[10] The degree of crystallinity of polystyrene blocks in copolymers, $f_{c(PS)}$, calculated by using the heat of fusion values of *i*-PS block, ranges from 36 to 42%.[8]

The crystallinity of both blocks renders this new material potentially very interesting for the expected physical properties. We are currently using this catalyst for the synthesis of new block copolymers with substituted styrene and other diene monomers and studying the mechanical proprieties of these new polymeric materials.

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Supporting Information Available: Polymerization procedures and plot of M_n and M_w/M_n versus conversion for butadiene polymerization using **1**/MAO and ^1H and ^{13}C of the block copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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